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Effects of CO₂ storage in coal on coal propertiesTshifhiwa Maphala^{a*}, Nicola J. Wagner^a*School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa, 2050*

Abstract

Unlike other storage options, CO₂ storage in coal seams is still in its infancy and requires advanced research to address the number of unknowns. One of the many questions that still need to be answered concerns the long term effects of storing CO₂ in coal, specifically on the structure and properties of the coal. Most studies on coal structural changes have been conducted over a short period of adsorption (hours or 2-3 days) and at low pressures (1-20 bar). Available literature has shown that the volumetric strains are a function of the local petrographic composition, and, in general, a coal's response to CO₂ sorption is based on the coal petrographic composition. The aim of this study was to determine any molecular structural and physical changes that may occur in coal following long term exposure (up to 6 months) to CO₂ under subcritical conditions (up to 42 bar). Inertinite-rich coal particles have a higher microporous surface area than vitrinite-rich particles of the same rank, as demonstrated by BET analysis. XRD results on the pre- and post-sorption coal samples demonstrated that CO₂ sorption in coal causes some structural changes. The structural changes were found to be different for coals of different maceral composition, confirming the initial hypothesis. The coal samples that were exposed to CO₂ over longer periods of time (6 months) displayed a more pronounced change in coal structure than those that were exposed for a shorter period of time (14 days). Volumetric sorption studies demonstrated that CO₂ treated vitrinite-rich particles have a greater change in sorption properties than inertinite-rich particles. The study provides an insight into the chemical and physical changes caused by sorption of CO₂ into coal, and could be used for modelling CO₂-coal interactions, and for assisting in CO₂-coal uptake calculations.

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Keywords: vitrinite, inertinite, XRD, coal structure, adsorption, CO₂ storage, CO₂

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1. Introduction

One of the options under consideration as a CO₂ mitigation strategy is the storage of CO₂ in unminable coal seams, with or without enhanced coal bed methane recovery. However, unlike conventional storage reservoirs, gas storage in coal seams is quite complex, mainly due to the extremely intricate and heterogeneous nature of the coal[1]. This complexity is evident in the many studies relating the interaction of CO₂ with coal, and has been an area of great interest recently[2-4]. However, there still much that is not understood about coal-CO₂ interactions [4-6].

A prime example of this knowledge gap is evident in one of the major hindrances to the deployment of CO₂ storage in coal seams; that is, the decrease in injectivity during CO₂ injection [7]. Although swelling has been identified as the prime culprit for this observation [8], little work has been done at a fundamental scientific level to understand the CO₂-coal interaction leading to this observed phenomenon. The little work that has been conducted on the subject has been done under conditions that do not truly represent those of potential storage sites; that is, the research has been conducted over short periods of adsorption (hours or 2-3 days) and mostly at low pressures [1-20bar].

To replicate actual in situ conditions in a laboratory is extremely difficult, and for the purposes of this research high pressure reactors capable to holding coal lumps were used. The current study was developed to take a more fundamental approach to understanding the effects of storing CO₂ in coal. This study aims to address the following fundamental research question with regards to CO₂-coal interactions: what is the long term (6 months) effect of CO₂ storage on the coal structure and properties? To address this question, chemical and physical changes following CO₂-coal interactions were considered for coals saturated with CO₂ for up to 6 months. The samples were selected from a density fraction of a South African coal, and were characterised pre-and post- treatment with CO₂. Whilst sub-and supercritical conditions were used in the research, this paper addresses the results from the sub-critical CO₂ adsorption experiments.

2. Samples, characterization and experimental

2.1. Samples

Coal samples were obtained as belt cuts from the Waterberg coalfield (numbered 14 in Fig. 1), Limpopo Province, South Africa (Fig. 1).

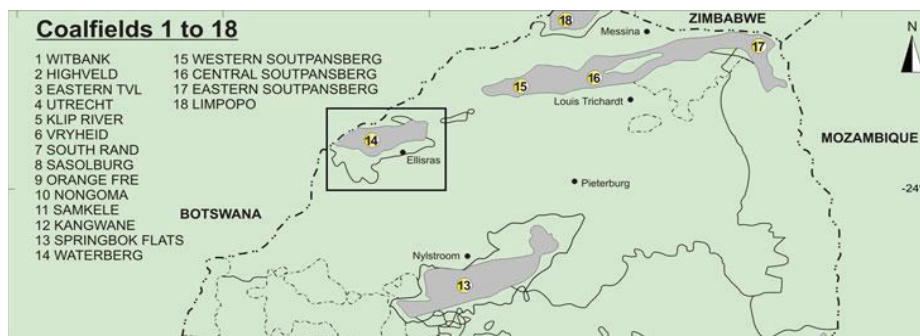


Fig 1: Map showing the location of the Waterberg coalfield, South Africa [9]

The samples were crushed and screened using a +500 μ m -1000 μ m size sieve and density separated using an organic solvent. The organic solvents used in this project were chloroform and benzene. Benzene has a specific gravity (S.G) of 0.88 and chloroform an S.G. of 1.48. The density separated samples were characterised before and after density fractionation using organic chemicals to ensure that there was no alteration of the coal by the density separating media. Table 1 shows the petrographic properties of the coals after separation; Coal A is a vitrinite- rich sample, and Coal B is inertinite-rich.

Table1: Petrographic analysis of the density fractionated samples (vol%)

Component	Coal A	Coal B
Vitrinite	91.8	11.2
Liptinite	2.6	3.8
Inertinite	2.2	80.2
Mineral matter	3.4	4.8
Rank	High volatile bituminous C coal	

Mineral matter content and rank is consistent between the samples, thus eliminating any variability in the results due to these parameters. Portions of the vitrinite and inertinite-rich samples were demineralised prior to CO₂ treatment to remove the interference of mineral matter during XRD analysis.

2.2. Characterisations

In order to determine any changes in the samples following the 6 month CO₂ treatment, the coals were characterized before and after exposure to CO₂ using the following advanced techniques: (i) Brunauer-Emmett-Teller (BET) method for the physical properties, (ii) Fourier-Transform Infrared (FTIR) Spectroscopy to probe for functional properties change, (iii) x-ray diffraction (XRD) to observe the internal crystalline structural changes, and (iv) a volumetric adsorption system to measure adsorption properties.

1. *BET* - CO₂ adsorption probe gases were used at 273 K. CO₂ is a necessary probe gas as it is able to access microporous regions potentially accessible by CO₂ during sequestration [10]. A Micrometrics ASAP 2010 Analyzer, housed at North-West University (South Africa) was used to perform the analysis
2. *FTIR* - spectra were obtained using a solid state Bruker FTIR spectrometer equipped with a NICPLAN microscope, housed at the University of the Witwatersrand (South Africa). A 35 x IR objective and an aperture of 30 μ m were used for micro-FTIR analyses, conducted in both transmission and reflected modes. All spectra were obtained at resolution of 4cm⁻¹ and 64 scans were co-added (a background of 64 scans was calculated). Bands were assigned according to Painter et al [11].
3. *XRD* - powder X-ray diffraction data were collected using a Bruker AXS D2, housed at the University of the Witwatersrand (South Africa). The equipment is equipped with a primary beam

Gobel mirror, a radial Soller slit, a V Antec-1 detector, using Cu-K radiation (40kV, 40mA). Data was collected in the 2θ range 5 to 90 in 0.007 steps, using a scan speed resulting in an equivalent counting time of 439.2s. Sample particle size was 50 μ m -150 μ m.

4. *Adsorption isotherms* - adsorption isotherms were obtained using a volumetric adsorption system, running up to pressures of 20MPa. The instrument consists of a gas storage vessel and an adsorption chamber, connected by a tube with an air controlled. Both vessels are placed within a thermostat (air) and provided with tubes for gas supply and evacuation, as well as with thermometers and manometers to measure the temperature and pressure inside the vessels [12]. The equipment is housed in the School of Chemical and Metallurgical Engineering, University of the Witwatersrand.

2.3. Experimental

Static pressure experiments were performed by exposing coal to CO₂ treated in reactors at different temperatures and pressures over varying periods of time. The samples were placed in both subcritical and supercritical conditions, but only subcritical conditions are reported in the paper. Table 2 shows the experimental conditions for CO₂ treatment

Table 2: Experimental conditions for CO₂ treatment

Temperature	Pressure units(bar)	Time(days)	Particle Size(μ m)	Weight (g)
20-30°C	45	14	500 -1000	5
20-30°C	42	180	500 -1000	20

The reactors were enclosed with a heating jacket to control the temperature of the reactors. They were also coupled with a PT 100 thermocouple and a pressure transducer. A displaying unit was used to monitor for leaks and any other irregularities that might have occurred in the period under study.

In order to study the internal structural changes using XRD, demineralised untreated coals were placed in the high pressure reactors for treatment with CO₂, together with non-demineralised coals.

3. Results and Discussion

3.1. Effect on the physical properties

The BET surface area (CO₂) analysis showed that Coal A (vitrinite-rich) and Coal B (inertinite rich) have surface areas typical of low rank bituminous coals. It is acknowledged that BET CO₂ surface area analysis may be a contentious subject [10], but it has been used here not necessarily as an measurement of surface area, but for comparison purposes between coal samples A and B.

When comparing the surface area of Coal A to that of Coal B, it was found that coal A had about 10% greater surface area than coal B (Fig. 2). The left bar in Fig. 2 is the non-treated surface area, and the right shows the result following 6 months treatment in CO₂ at 42 bar. The treated vitrinite-rich coal (A) shows a significantly higher surface area than its non-treated counterpart. The inertinite sample shows no significant change after treatment.

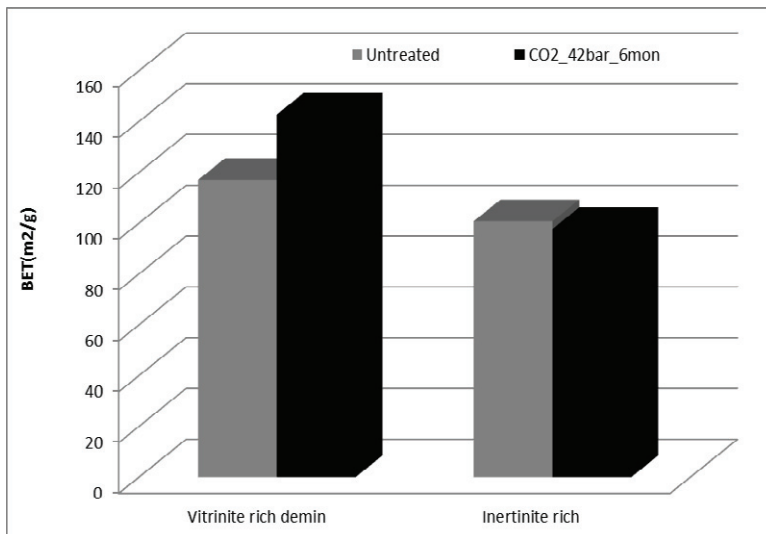


Fig 2: BET CO₂ surface area for non-treated and 6 months treated coals

A possible explanation for the change in surface area is: (i) a change in the pore structure of the coal structure due to the long term CO₂ sorption; and/or (ii) CO₂ imbibition into the coal structure. To further investigate the cause of the surface area change, the pore size distribution for the coals was analysed. The CO₂ sorption/desorption data was used to calculate pore size distribution (PSD) using the Horvath – Kawazoe method [13]. Fig. 3a shows for the microporous region of Coal A (vitrinite rich), and Fig 3b the microporous region for Coal B (inertinite-rich).

An observation that one can make is that the two samples seem to have fairly similar microporous PSDs, though they have different petrographic composition. For both Coal A and Coal B, the 6 months treated coals show a greater PSD distribution than the untreated coals. This would suggest that some structural deformation might have occurred due to the long term CO₂ treatment period.

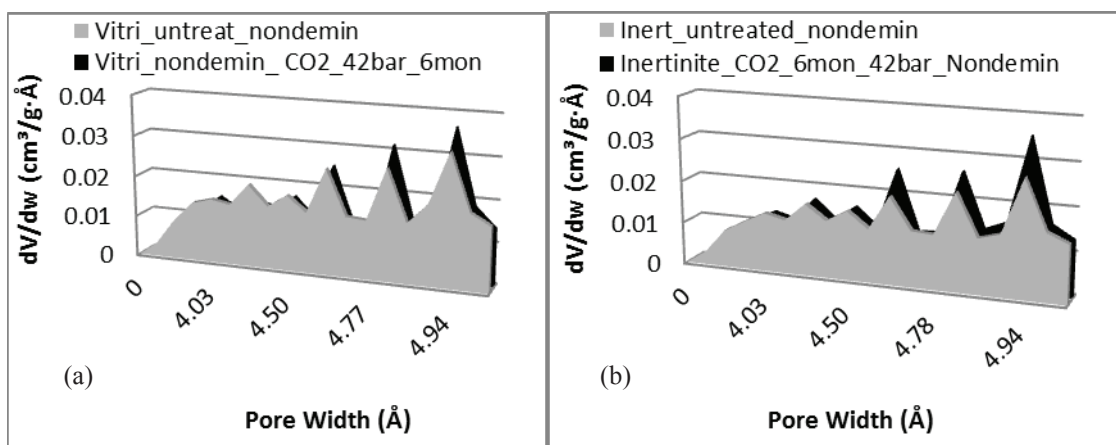


Fig 3: PSD analysis for the two different coal samples. (a) Coal A (Vitrinite-rich) and (b) Coal B (Inertinite-rich)

It is possible to deduce structural deformation from PSD's, following Kowalczyk et al [14]. In this study [14], adsorption induced deformation of carbon materials is dependent on the pore size distribution. Small pores of width $<0.38\text{nm}$ (i.e., slightly wider than adsorbate molecular diameter of 0.34 nm) swell the carbon material, whilst the larger pores ($>0.38\text{ nm}$) contract the material.

Caution must be exercised when utilizing the sorption/desorption data to deduce a PSD for microporous carbonaceous materials such as coals, as there is still some theoretical uncertainties associated with these methods. There is, however, still value in comparing PSDs for structural characterisation purposes as was done in the above paragraph [15]. It can be deduced from the above observations that there are physical changes on the pore structure and the surface area of the coal following by CO_2 sorption over 6 months.

3.2. Effect on the chemical properties

Since CO_2 has polar bonds and a large quadrupole moment, specific chemical interactions between coal and CO_2 may make an important contribution to the adsorption process, one which may well significantly alter the surface functional composition of the coal and its subsequent behavior [16].

To test this, FTIR analysis of treated and untreated samples was performed to qualitatively observe if the CO_2 treated at conditions in this study resulted in any significant surface functionality changes. Fig. 4 shows the FTIR spectra of the treated and untreated Coal A (vitrinite-rich) samples.

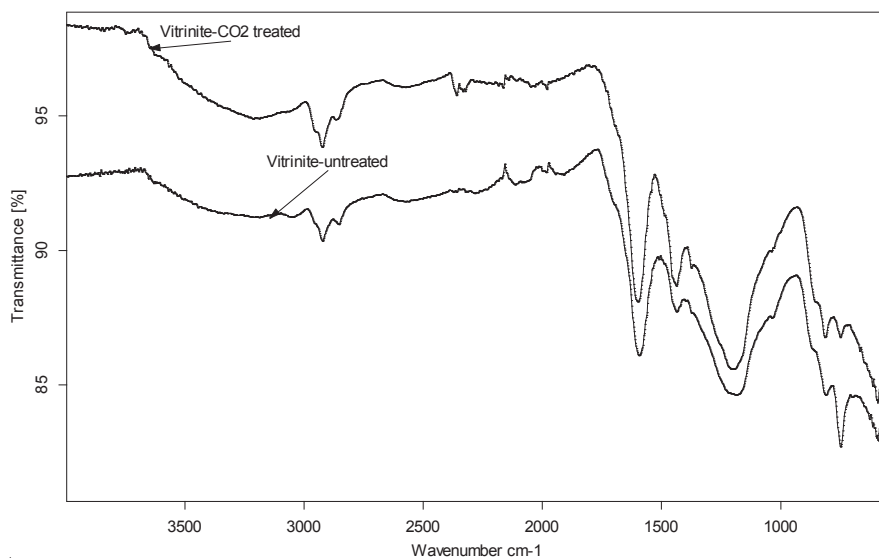


Fig 4: An FTIR spectra of treated and untreated Coal A (vitrinite-rich) samples

Of particular interest for the current study were the hydroxyl group ($3200\text{--}3600\text{cm}^{-1}$) and the adsorbed CO_2 peak at 2330cm^{-1} . As stated in Saikai et al [17], the amount of CO_2 adsorbed per square meter of the surface area and the heat of CO_2 adsorption increases with an increase in the fraction of the surface covered by hydroxyl groups [17]. Consequently, a high hydroxyl group on the surface would induce a higher CO_2 adsorption. Of greater interest to this study is whether this interaction would cause any functionality changes on the surface of the coal.

As shown in Fig. 4, the hydroxyl group peak ($3000\text{--}3500\text{cm}^{-1}$) shows no changes between the treated and untreated vitrinite-rich samples. In addition, the only difference between the two peaks is the change in the peaks between 2000cm^{-1} and 2500cm^{-1} . Although the region is a fingerprint for other functional groups, the notable difference is with the adsorbed CO_2 peak region at 2330cm^{-1} [18]. Goodman et al [2] showed that absorbance intensity of the CO_2 peak was time-dependent, and increased with the length of CO_2 exposure. Goodman et al's study showed that if CO_2 is initially sorbed into the coal structure and released, as in our study, the coal structure structural rearrangement occurs after the initial uptake. The rearrangement is not reversed as the CO_2 is removed from the coal. A similar peak increase was observed in this study, which is an indication of structural rearrangement, although not quantified here.

3.3. Effects on the internal structure

Coal has a very complex internal structure [19–22], and this complexity makes it challenging to study the internal structural changes due to CO_2 sorption without making certain assumptions. Without delving too much into the coal structure and its complexities, it should suffice to state that here the internal structure refers to the crystalline structure of the coal.

Analysis of the internal structure was performed on demineralised untreated, 14 days, and 6 months treated coals. The 14 day analysis was included in this section as it enabled statistically valid correlations

to be drawn from the d_{002} and L_c data in Fig. 5 (discussed later). A pre-sorption solid state ^{13}C NMR analysis of the coals showed that Coal B (inertinite rich) had a higher fraction of aromatic carbons than Coal A (vitrinite rich) sample, as expected. In order to study the internal structural changes, demineralised and untreated coals were saturated with CO_2 , together with non-demineralised coals, as discussed in the experimental section (§2.3). Powder XRD patterns for Coal B untreated, treated for 14 days at 45 bar, and 6 months at 42 bar, are shown in Fig. 5.

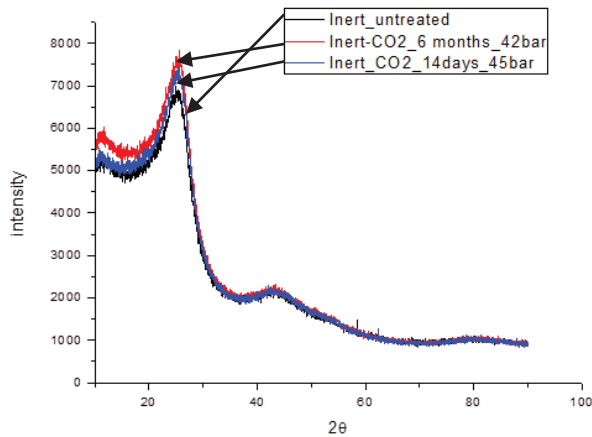


Fig 5: Powder XRD patterns for the untreated, 14 days treated, and 6 months treated inertinite-rich coal

The most prominent band in an XRD diffractogram pattern of coal is the (002) band at about 2θ 23° , because it arises from the parallel stacking of planar (d_{002}) aromatic ring clusters. It is also well established that the (002) peak position changes with carbon content [23-25]. In this study, it was postulated that, if CO_2 sorption at high pressures affected the internal structure of the coal, then the peak position and intensity of the (002) band can be used to observe, and, if possible, measure the degree of change in the parallel stacking of planar aromatic clusters. Only Coal B is shown, because Coal A had a lower fraction of aromatic carbon and it was difficult to observe the d_{002} band.

From the XRD data the interlayer spacing between the aromatic rings can be determined. This is done by calculating the interlayer distance between aromatic sheets (d_{002}) from a maximum of the (002) band using the Bragg equation {Document not in library: [26]} .

$$d_{002} = \lambda / 2 \sin \theta_{002} \quad (1)$$

The average crystallite stacking height (L_c) can be computed:

$$L_c = 0.9 \lambda / \beta_{002} \cos \theta_{002} \quad (2)$$

Where β_{002} is the integral breadth or breadth at half maximum intensity of the pure reflection profile in radians, θ_{002} is the angle 002 angle, and λ is the copper wavelength, 1.54nm. Results for the calculation of these structural parameters are shown in Fig. 6. Evident from the Fig 6 is the fact that the inter-planar d_{002} spacing between the samples is unchanged for the untreated, 14 days treated, and the 6 months CO_2 treated coals. This was because the d_{002} peak position did not change with CO_2 saturation. However, the

average stacking height of the aromatic fringes in the coal seem to be increasing from untreated, 14 days treatment, to 6 months treatment.

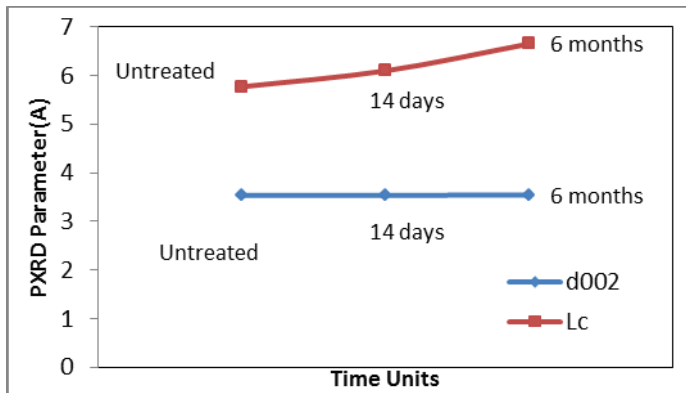


Fig 6: Structural parameters from powder XRD analysis for treated and untreated coal B.

From a structural point of view, an increase in the stacking height corresponds to an increase or opening of slit-shaped micropores, considering the fact that micropores of this type are basically formed by a misconfiguration among layers or stacks [27]. This observation would help explain the sorption properties observed in the PSD changes and next section.

3.4. Effects on the sorption properties

Sorption properties for the CO₂ saturated and unsaturated samples were tested using a volumetric adsorption system. The tests were done to determine whether the surface area and pore structural changes observed would have a significant change in the sorption properties of the coal. Additionally, the tests were performed to assess whether these changes would differ according to the maceral composition of the coals.

Fig. 7 shows the CO₂ excess adsorption against relative pressure. The untreated coal A (vitrinite-rich) had a higher adsorption capacity than coal B (inertinite-rich), as expected. What is clearly evident is that the treatment in CO₂ for 6 months did affect the absorption capacity in these samples. Coal B untreated shows a different isothermal behaviour compared to the 6 month treated sample. Coal B untreated shows a Type I isotherm reaching a limiting value at higher partial pressures, whereas coal B after 6 months shows an isotherm similar to Type III isotherm, which can be considered to be unusual for coals.

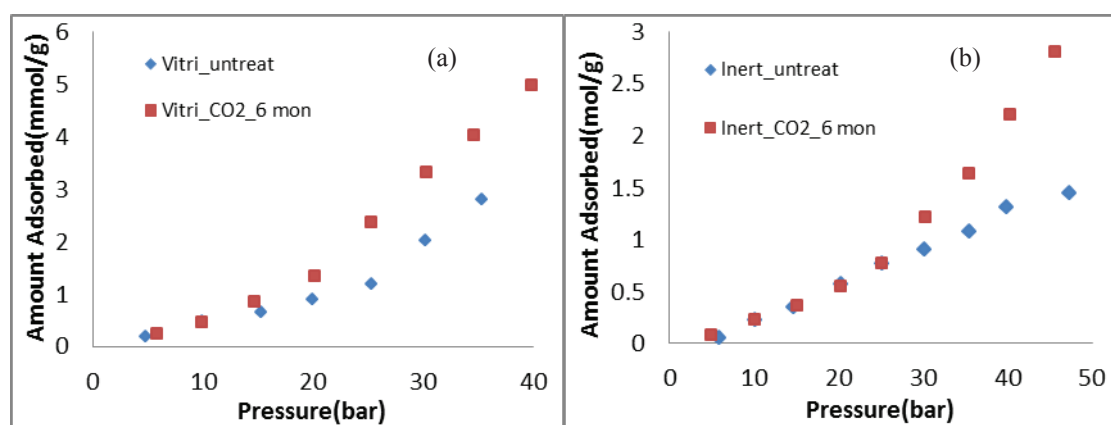


Fig. 7: Excess Adsorption isotherms for treated and untreated (a) coal A and (b) coal B

Another interesting observation from Fig. 7 is the shape of the isotherms for Coal A. On initial observation, Coal A has a Type III adsorption isotherm for both treated and untreated samples (assuming pure physical adsorption has taken place). Isotherms of this type are not common [28]. To assume pure physical adsorption at these pressures, the isotherms would be erroneous since coal has been shown to display both adsorption and absorption. Therefore, it is suspected that another phenomenon could explain the shape of the adsorption isotherm. An alternative explanation for this type of isotherm is the loss in pore integrity due to the high pressure CO₂ treated for the long periods under study. This theory would also explain the deviation observed for both coal A and B treated samples at pressures greater than 0.3-0.4 partial pressures (15-30 bar). At these pressures, the effect of CO₂ on coals would be similar to the “conditioning effect” observed in glassy polymer-liquid sorbate systems. For glassy polymers the “conditioning effect” has been demonstrated for small molecules like CO₂ [29].

In the conditioning effect, pore deformation is brought about by the infusion of the sorbate into the sorbent at a concentration above the glass transition concentration of the sorbate. In this solid-liquid sorption system, conditioning first converts the sample to the rubbery state through the effect of plasticisation and causes the pores to disappear. Then, as the conditioning agent is removed and glass

transition concentration is approached from the high-concentration side, “new pores” are created in the solid. This leaves the conditioned sample with a greater pore capacity than the original sample. By this mechanism, the sorbate causes irreversible changes in the structure of internal micropores (holes) in the organic matrix upon its sorption [30,31]. If it is assumed that the experimental conditions under study, this transition concentration was reached, then the theory does explain the observed sorption behaviour.

4. Conclusion and future work

This study was undertaken to determine, at a fundamental level, the chemical and physical changes caused by CO₂ sorption in coal after 6 months of treatment. BET analysis of treated and untreated coals showed that the vitrinite-rich coal samples have a greater surface area and change in pore structure than the inertinite-rich coal samples used in this study. Functional group analysis indicated that there was no functionality change for the treated and untreated coals. Analysis of the crystalline part of the CO₂ treated and untreated inertinite-rich samples showed that there was slight increase in the average crystallite height, although no changes were observed for the d_{002} aromatic interplanar spacing. The study determined that there was a significant increase in the sorption capacity of the treated coals compared to the untreated, petrographically comparable samples, and that the increase occurs at specific pressure points (15 and 30bar) for each petrographic type. The work on assessing the effect of treatment at supercritical pressures over 6 months is continuing.

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